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THERMODYNAMICS OF AN OSCILLATOR ASSEMBLY

By R. P. SINGH

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ABSTRACT. The thermodynamics of an assembly of linear harmonic oscillators is worked out. The expressions for specific heat obtained here for Bose and Fermi statistics are compared with those of Auluck and Kothari. Their results, obtained by use of partition theory of numbers, show that entropy and hence the specific heat is the same for both B E and F D cases while here it is approximately the same, and not exactly In the derivation here the sums have been replaced by integrals and it remains to investigate where the difference actually lies in the two cases This will be done in the next communication

The thermodynamical study of an assembly of linear oscillators is of considerable intrinsic interest, and also because of its close connection, as has been shown by Auluck and Kothari (1946), with the partition theory of numbers In fact, one can profitably discuss processes of approximation, replacement of sums by integrals and so on for this assembly, and such a discussion is expected to furnish greater insight into these questions than one relating to a more complicated assembly. Further an examination of such questions is opportune as appears from Dingle's (1941) recent contribution.

We first take the case where the sums have been replaced by integrals in the usual manner. The distribution law of the assembly is

$$f(\epsilon)=\frac{1}{\frac{e^{\epsilon/kT}}{A}+\beta} \qquad \ldots \quad (1)$$

where $\beta=+1$ for Fermi-Dirac case and $\beta=-1$ for Bose-Einstein case, and

$$n(\epsilon)\ d\epsilon=a\ (\epsilon)\ f\ (\epsilon)\ d\epsilon$$

$$=\frac{a\ (\epsilon)\ d\epsilon}{\frac{e^{\epsilon/kT}}{A}+\beta} \qquad \ldots \quad (2)$$

with

$$N=\int_0^\infty n\ (\epsilon)\ d\epsilon, \qquad \ldots \quad (3)$$

and

$$E=\int_0^\infty \epsilon n\ (\epsilon)\ d\epsilon. \qquad \ldots \quad (4)$$

For our case $\quad a\ (\epsilon)=\frac{1}{\hbar\omega}$

so for N and E we have

$$N = \frac{kT}{\hbar\omega} \int_0^\infty \frac{du}{\frac{e^u}{A} + \beta} \quad \ldots \quad (5)$$

and

$$E = \frac{(kT)^2}{\hbar\omega} \int_0^\infty \frac{u\,du}{\frac{e^u}{A} + \beta} \quad \ldots \quad (6)$$

where

$$u = \frac{\epsilon}{kT} .$$

1. For the case of non-degeneracy we have $A << 1$ and the distribution function is easily expanded as series. In this case the total number N of the oscillators in the assembly is given by

$$A_1 = \sum \frac{A^n}{n} (-\beta)^{n-1} \quad \ldots \quad (7)$$

where A_1 is defined by $A_1 = \frac{N\hbar\omega}{kT}$.

In above equation (7) a quantity A_1 has been defined and $\beta = -1$ for Bose-Einstein case and $\beta = +1$ for Fermi-Dirac case. The total energy of the assembly is given by

$$E = \frac{(kT)^2}{\hbar\omega} \int_0^\infty \frac{u\,du}{\frac{e^u}{A} + \beta}$$

$$= NkT\{1 + a\beta A_1 - b\beta^2 A_1^2 + c\beta^3 A_1^3 + \ldots\} \quad \ldots \quad (8)$$

where $a = \frac{1}{2^2}, \; b = \left(\frac{2}{3^2} - 1\right)$

and $c = \frac{3}{4^2} + \frac{5}{2.8} - \frac{3}{6}$.

Substituting the value of A_1 we get for the energy of the assembly,

$$E = NkT + a\beta N^2\hbar\omega - b\beta^2 \frac{N(N\hbar\omega)^2}{kT} + c\beta^3 N\frac{(N\hbar\omega)^3}{(kT)^2} + \quad \ldots \quad (9)$$

and the specific heat of the assembly is given by

$$C_v = \frac{\delta E}{\delta T} = Nk\left[1 + b\beta^2\left(\frac{N\hbar\omega}{kT}\right)^2 - 2c\beta^3\left(\frac{N\hbar\omega}{kT}\right)^3 + \ldots \quad \ldots \quad (10)\right.$$

The thermodynamical potential and the entropy of the assembly can also be obtained as follows for the non-degenerate case. They are

$$\frac{G}{NkT}=\log A=\log A_1+2a\beta A_1-\tfrac{3}{2}b\beta^2A_1^2+\tfrac{4}{3}c\beta^3A_1^3+\ \ldots \tag{11}$$

and

$$\frac{S}{Nk}=\frac{E-G}{NkT}=1-\log A_1-a\beta A_1+\tfrac{1}{2}b\beta^2A_1^2-\tfrac{1}{3}c\beta^3A_1^3\ \ldots \tag{12}$$

or

$$S=Nk[1-\log A_1+a\beta A_1+\tfrac{1}{2}b\beta^2A_1^2-\tfrac{1}{3}c\beta^3A_1^3+\ldots] \tag{13}$$

In the above G is the thermodynamic potential of the assembly and S is the entropy and again $\beta=+1$ corresponds to F. D. case and $\beta=-1$ to thd B. E. case

The equation (10) demonstrates an interesting fact, that is, it shows that for non-degeneracy ($A<<1$) the specific heat C_v of the assembly is proportional to the number of oscillators in it and that it is the same for both Bose-Einstein and Fermi-Dirac cases to the approximation of the order of $\left(\frac{N\hbar\omega}{KT}\right)^2$.

2. We shall now take up the degenerate case

In degeneracy the Fermi-Dirac and Bose-Einstein cases are considered separately. For Bose-Einstein degeneracy $A=1$ and $\beta=-1$ and so the energy of the assembly is,

$$E=\frac{(kT)^2}{\hbar\omega}\int_0^\infty\frac{udu}{e^u-1}=\frac{\pi^2}{6}\cdot\frac{(kT)^2}{\hbar\omega}.$$

Hence

$$C_v=\frac{\delta E}{\delta T}=\frac{\pi^2}{3}k\left(\frac{kT}{\hbar\omega}\right). \tag{15}$$

Also

$$G=NkT\log A=0, \tag{16}$$

and

$$S=\frac{E}{NkT}=\frac{\pi^2}{6}\cdot\frac{kT}{N\hbar\omega}=\frac{\pi^2}{6A_1}. \tag{17}$$

The degenerate case of Fermi-statistics is characterised by $A>>1$ and $\beta=+1$. In this case the integration is carried out by using Sommerfeld formula according to which for large A we have an asymptotic series expansion for the integral

$$\int_0^\infty\frac{d\phi(\epsilon)}{d\epsilon}\ \frac{1}{e^{\frac{\epsilon-\xi}{kT}}-1}\ d\epsilon \tag{18}$$

$$= \{\phi(\epsilon) + 2C_2\phi^{II}(\epsilon)(kT)^2 + 2C_4(kT)^4\phi^{IV}(\epsilon) + \ldots\}_{\epsilon=\xi} \qquad \ldots \quad (18a)$$

where

$$C_{2n} = (1 - 2^{1-2n})\zeta(2n) \qquad \ldots \quad (18b)$$

$\zeta(2n)$ being the well known Riemann-Zeta function. The numerical values of C_{2n} are (Mc-Dougall and Stoner, 1938)

$$C_2 = \frac{\pi^2}{12}, \; C_4 = \frac{7\pi^4}{720}$$

and

$$C_6 = \frac{31\pi^6}{30240}.$$

The above expansion of (18) is subject to an error of the order of $e^{-\xi/kT}$ and holds good if $\xi/kT >> 1$ and $\phi(\epsilon)$ is a regular function vanishing for $\epsilon = 0$.

We have in this case for N the number of oscillators in the assembly

$$N = \frac{1}{\hbar\omega}\int_0^\infty \frac{1}{e^{\frac{\epsilon-\xi}{kT}}+1}\, d\epsilon$$

$$= \frac{1}{\hbar\omega}\int_0^\infty \frac{d(\epsilon)}{d\epsilon} \cdot \frac{1}{e^{\frac{\epsilon-\xi}{kT}}+1}\, d\epsilon$$

$$= \frac{1}{\hbar\omega}\Big[\epsilon\Big]_{\epsilon=\xi} = \frac{\xi}{\hbar\omega}$$

$$= \frac{kT}{\hbar\omega}\log A \qquad \ldots \quad (19)$$

or

$$\frac{N\hbar\omega}{kT} = A_1 = \log A. \qquad \ldots \quad (20)$$

On the other hand the integral for N can be directly evaluated giving correct value of A_1. We have

$$A_1 = \int_0^\infty \frac{du}{\frac{e^u}{A}+1}.$$

putting $e^u = Z$ and changing the variable from U to Z we get

$$A_1 = \int_1^\infty \frac{dZ}{Z\left(\frac{Z}{A}+1\right)}$$

$$= \int_1^\infty \left[\frac{1}{Z} - \frac{1}{Z+A}\right] dZ$$

$$=\left[\log \frac{Z}{Z+A}\right]_1^{\infty}$$

$$=\left[-\log \frac{1}{1+A}\right]$$

$$=\log (1+A). \qquad \ldots (21)$$

Thus we have $\log (1+A)$ for the accurate value of A_1 which can be put in the form of a series in powers of A

$$\log (1+A)=\log A+\log\left(1+\frac{1}{A}\right)$$

$$=\log A+\frac{1}{A}-\frac{1}{2A^2}+ \qquad \ldots (27$$

and because $A>>1$ we have $\log (1+A) \sim \log A$, *i.e.* $A_1 \sim \log A$ which is the same result as (20).

Now the energy in the Fermi-Dirac case is

$$E=\frac{1}{\hbar\omega}\int_0^{\infty}\frac{\epsilon\, d\epsilon}{e^{\frac{\epsilon-\xi}{kT}}+1}$$

$$=\frac{1}{\hbar\omega}\int_0^{\infty}\frac{d(\frac{1}{2}\epsilon^2)}{d\epsilon}\cdot\frac{1}{e^{\frac{\epsilon-\xi}{kT}}+1}\,d\epsilon$$

$$=\frac{1}{\hbar\omega}\left[\tfrac{1}{2}\epsilon^2+2C_2\,(kT)^2\right]_{\epsilon=\xi}$$

$$=\frac{1}{\hbar\omega}\left[\tfrac{1}{2}\xi^2+\frac{\pi^2}{6}(kT)^2\right] \qquad (23)$$

We shall now find ξ using (21) and substitute in (23) for various orders of approximation.

To the zeroeth order approximation $A_1=\log A$

or $$A=e^{\frac{N\hbar\omega}{kT}}$$

but $$A=e^{\xi/kT} \text{ and so } \xi/kT=\frac{N\hbar\omega}{kT}$$

or $$\xi=N\hbar\omega. \qquad \ldots (24)$$

The energy E in this case is

$$E=\frac{1}{\hbar\omega}\left[\tfrac{1}{2}(N\hbar\omega)^2+\frac{\pi^2}{6}(kT)^2\right] \qquad \ldots (25)$$

$$=\tfrac{1}{2}N^2\hbar\omega+\frac{\pi^2}{6}\cdot\frac{(kT)^2}{\hbar\omega}$$

and so
$$C_v=\frac{\delta E}{\delta T}=\frac{\pi^2}{3}k\left(\frac{kT}{\hbar\omega}\right) \quad \ldots \quad (26)$$

Here we see that we have got equation (26) identical with (15) for the Bose-Einstein case. Thus to a zeroeth order approximation the specific heat is the same for both Bose-Einstein and Fermi-Dirac cases for degeneracy. The specific heat is seen to be independent of the number of oscillators in the assembly for the Fermi-Dirac case That it is also the same for Bose-Einstein case is easily understandable.

$$C_v=\frac{\pi^2}{3}k.\left(\frac{kT}{\hbar\omega}\right) \text{ exactly for Bose case}$$

and
$$C_v=\frac{\pi^2}{3}k\left(\frac{kT}{\hbar\omega}\right) \text{ approximately for F. D case.}$$

We now proceed to obtain the value of C_v in the present case to a higher approximation using more accurate value of ξ.

From equation (21) we have again

$$\frac{N\hbar\omega}{kT}=\log\,(1+A)$$

or
$$A=e^{\frac{Nh\omega}{2\pi kT}}-1$$

and hence
$$e^{\xi/kT}=e^{\frac{Nh\omega}{2\pi kT}}-1$$

i.e.,
$$\xi/kT=\log\,e^{\frac{Nh\omega}{2\pi kT}}+\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)$$

$$=\frac{N\hbar\omega}{kT}+\log\left(1-e^{\frac{Nh\omega}{2\pi kT}}\right),$$

which gives
$$\xi=N\hbar\omega+kT\log\left(1-e^{\frac{-Nh\omega}{2\pi kT}}\right), \quad \ldots \quad (27)$$

and
$$\xi^2=(N\hbar\omega)^2+2N\hbar\omega kT\,\log\left(1-e^{\frac{-Nh\omega}{2\pi kT}}\right)+(kT)^2\left\{\log\left(1-e^{\frac{-Nh\omega}{2\pi kT}}\right)\right\}^2.$$

Substituting this value of ξ^2 in (23), we get

$$E=\frac{1}{\hbar\omega}\left[\frac{1}{2}\left\{(N\hbar\omega)^2+2N\hbar\omega kT\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)\right.\right.$$

$$\left.\left.+(kT)^2\left(\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)\right)^2\right\}+\frac{\pi^2}{6}(kT)^2\right]$$

$$=\frac{N^2\hbar\omega}{2}+2NkT\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)$$

$$+\frac{(kT)^2}{\hbar\omega}\left[\frac{\pi^2}{6}+\left\{\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)\right\}^2\right]$$

and hence the specific heat C_v is

$$C_v=\frac{\delta E}{\delta T}=2Nk\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)-\frac{\frac{2N^2\hbar\omega}{T}e^{-\frac{Nh\omega}{2\pi kT}}}{1-e^{-\frac{Nh\omega}{2\pi kT}}}$$

$$+\frac{2k(kT)}{\hbar\omega}\left[\frac{\pi^2}{6}+\left\{\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)\right\}^2\right]$$

$$-\frac{(kT)^2}{\hbar\omega}\cdot\frac{\frac{2N\hbar\omega}{kT^2}e^{-\frac{Nh\omega}{2\pi kT}}\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)}{1-e^{-\frac{Nh\omega}{2\pi kT}}} \qquad \ldots (29)$$

or

$$C_v=\frac{\pi^2}{3}k\left(\frac{kT}{\hbar\omega}\right)+2Nk\left\{1-\frac{1}{e^{\frac{Nh\omega}{2\pi kT}}-1}\right\}\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)$$

$$-\frac{2N^2\hbar\omega}{T}\cdot\frac{1}{e^{\frac{Nh\omega}{2\pi kT}}-1}+\frac{2k(kT)}{\hbar\omega}\left\{\log\left(1-e^{-\frac{Nh\omega}{2\pi kT}}\right)\right\}^2 \qquad \ldots (30)$$

Equation (30) shows that in the degenerate Fermi-Dirac case the specific heat has additional terms beyond $\frac{\pi^2}{3}k\left(\frac{kT}{\hbar\omega}\right)$. It can be seen that these terms have a very small contribution to specific heat. But on the other hand if we proceed by more exact method of sums (and not replace by integrals) as described by Auluck and Kothari (1946), we find that entropy and hence specific heat is exactly the same for Bose and Fermi statistics.

The above treatment shows that we get results by integral method which do not agree exactly with those obtained by sum method. It would be of interest to investigate where the difference actually lies and in this connection the work of Dingle and Liebfried and Kaempffer (1948) is relevent.

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DEPARTMENT OF PHYSICS
UNIVERSITY OF ALLAHABAD.

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